

CIRCULARLY POLARIZED LIGHT-INDUCED AXIAL ANISOTROPY IN ACHIRAL ISOTROPIC MEDIA. MAGNETIC DIPOLE INTERACTION WITH RADIATION

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The analytical explanation of axial birefringence revealed earlier by the technique of field applied molecular dynamics computer simulation is given. The point group symmetries of achiral molecules admitting the effect are determined and the estimation of the anisotropy is presented. The effect may give information on off-diagonal elements of the Rosenfeld polarizability tensor of achiral molecules.

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1. Introduction

Various optical birefringences can be induced in isotropic media by a static electric or magnetic field, among them there is the Kerr effect and the Cotton-Mouton effect [1-5], the Faraday effect [6, 7] and magnetochiral birefringence [8-13]. The birefringence can also be induced by these two static fields applied simultaneously [14-18], an electric field gradient [19] or by a high intensity optical beam [3, 20-25].

Recently [26] the technique of field applied molecular dynamics (FMD) computer simulation has been used to show the existence of a novel anisotropy induced by circularly polarized (c.p.) light in media composed of chiral or achiral molecules. In that paper two real torques acting on a molecule in the presence of c.p. light were taken into consideration:

$$\mathbf{T}_1 = \frac{1}{2} \boldsymbol{\mu} \times \mathbf{E}^* + \text{c.c.}, \quad (1)$$

$$\mathbf{T}_2 = \frac{1}{2} \mathbf{m} \times \mathbf{B}^* + \text{c.c.}, \quad (2)$$

where $\boldsymbol{\mu}$ is the electric dipole moment induced in a molecule by the magnetic field \mathbf{B} of the c.p. light and \mathbf{m} is the magnetic dipole moment induced by the electric field \mathbf{E} of the c.p. light (\mathbf{E}^* and \mathbf{B}^* denote the complex conjugates of \mathbf{E} and \mathbf{B}).

The torques (1) and (2) lead to the light intensity dependent axial birefringence for chiral as well as achiral molecules possessing appropriate symmetries, as was shown by the FMD technique for (S)-CHBrClF and H₂O, respectively [26].

Additional contributions to the effect due to electric quadrupole interaction with electromagnetic radiation are in general comparable with the magnetic dipole contributions and they will be presented in a separate paper.

2. The basic formulae

We consider an isotropic molecular system in which a monochromatic light wave with the electric field

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{2} \mathbf{E}(\omega, \mathbf{k}) \exp \left[-i\omega \left(t - \frac{n}{c} \mathbf{r} \cdot \mathbf{s} \right) \right] + \text{c.c.} \quad (3)$$

propagates in the \mathbf{s} -direction, n is the light refractive index, \mathbf{k} — the propagation vector of the wave, and c — the velocity of light in vacuum.

The optical properties of liquid and gaseous media composed of non-interacting molecules are described by the material equations for the electric \mathcal{D} and magnetic \mathcal{B} flux density:

$$\mathcal{D}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{B}) = \varepsilon_0 \mathbf{E}(\omega, \mathbf{k}) + N \langle \boldsymbol{\mu}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{B}) \rangle_{\mathbf{E}, \mathbf{B}}, \quad (4)$$

$$\mathcal{B}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{B}) = \mu_0 \mathbf{H}(\omega, \mathbf{k}) + \mu_0 N \langle \mathbf{m}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{B}) \rangle_{\mathbf{E}, \mathbf{B}}, \quad (5)$$

where $\boldsymbol{\mu}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{B})$ and $\mathbf{m}(\omega, \mathbf{k}, \mathbf{E}, \mathbf{B})$ are the electric dipole and magnetic dipole moment, respectively, induced in the molecule by the fields \mathbf{E} and \mathbf{B} of the light, N is the number of molecules per unit volume, ε_0 and μ_0 — the electric and magnetic permittivity of vacuum, and the symbol $\langle \dots \rangle_{\mathbf{E}, \mathbf{B}}$ stands for the space average in the presence of the fields \mathbf{E} and \mathbf{B} ; $\mathbf{H}(\omega, \mathbf{k}) = \mu_0^{-1} \mathbf{B}(\omega, \mathbf{k})$ is the magnetic field of the light.

Since we are interested in the analytical explanation of the optical anisotropy of the medium due to the torques (1) and (2), we will take now into consideration only optically induced reorientational processes giving any contribution to the refractive index. The induced dipole moments $\boldsymbol{\mu}$ and \mathbf{m} oscillating with the frequency ω can be written in the following approximation:

$$\mu_i(\omega, \mathbf{E}, \mathbf{B}) = {}^e \alpha_{ij}^e(-\omega; \omega) E_j + {}^e \alpha_{ij}^m(-\omega; \omega) B_j, \quad (6)$$

$$m_i(\omega, \mathbf{E}, \mathbf{B}) = {}^m \alpha_{ij}^e(-\omega; \omega) E_j, \quad (7)$$

where ${}^e \alpha^e(-\omega; \omega)$ and ${}^e \alpha^m(-\omega; \omega)$ is the electric dipole polarizability related to dipolar-electric and dipolar-magnetic transitions, respectively, ${}^m \alpha^e(-\omega; \omega)$ is the magnetic dipole polarizability related to dipolar-electric transitions (the electric quadrupole interaction with radiation is not considered here and it will be presented in a separate paper).

The space average in the presence of the electromagnetic field can be carried out using the formula [3]:

$$\langle \Phi \rangle_{\mathbf{E}, \mathbf{B}} = \langle \Phi \rangle - \frac{1}{k_B T} (\langle \Phi U \rangle - \langle \Phi \rangle \langle U \rangle) + \dots, \quad (8)$$

where k_B is the Boltzmann constant, T — the temperature, and U — the potential energy of the molecule in the presence of the laser beam:

$$U = -\frac{1}{2} {}^e\alpha_{ij}^e(-\omega; \omega) E_i^* E_j - \frac{1}{2} {}^e\alpha_{ij}^m(-\omega; \omega) E_i^* B_j - \frac{1}{2} {}^m\alpha_{ij}^e(-\omega; \omega) B_i^* E_j + \text{c.c.} \quad (9)$$

In general, for molecules with complex wave functions, the polarizabilities ${}^e\alpha^e$, ${}^e\alpha^m$ and ${}^m\alpha^e$ can be represented as follows (from here on we will not indicate anymore the frequency in the symbols of the polarizabilities, writing α instead of $\alpha(-\omega; \omega)$):

$${}^e\alpha_{ij}^e = {}^e\beta_{ij}^e + i {}^e\gamma_{ij}^e = {}^e\beta_{ji}^e - i {}^e\gamma_{ji}^e, \quad (10)$$

$${}^e\alpha_{ij}^m = {}^e\beta_{ij}^m + i {}^e\gamma_{ij}^m, \quad (11)$$

$${}^m\alpha_{ij}^e = {}^m\beta_{ij}^e + i {}^m\gamma_{ij}^e = {}^m\beta_{ji}^m - i {}^m\gamma_{ji}^m, \quad (12)$$

where the tensor components ${}^e\beta_{ij}^e$, ${}^e\gamma_{ij}^e$, ${}^e\beta_{ij}^m$, ${}^e\gamma_{ij}^m$, ${}^m\beta_{ij}^e$ and ${}^m\gamma_{ij}^e$ are real in the absence of absorption with the quantum mechanical forms given in Ref. [8]. For molecules with real wave functions the tensor components ${}^e\gamma_{ij}^e$, ${}^e\beta_{ij}^m$ and ${}^m\beta_{ij}^e$ are equal to zero [8, 27, 28].

On transforming the material Eqs. (4) and (5) to circular basis and on solving them in this basis jointly with the Maxwell equations we obtain expressions defining the refractive indices n_+ and n_- for right and left c.p. light, respectively, propagating in the z -direction of the laboratory frame of coordinates $\{X, Y, Z\}$ in a medium composed of achiral molecules

$$n_{\pm} = n_0 + n_T^{\text{NL}} |E|^2 \pm F_T i(\mathbf{E} \times \mathbf{E}^*)_z \pm D_T i(\mathbf{E}^* \cdot \mathbf{B}) + M_T (\mathbf{E}^* \times \mathbf{B})_z, \quad (13)$$

where

$$n_0 = \left(1 + \frac{N}{\varepsilon_0} {}^e\beta^e\right)^{1/2} \quad (14)$$

is the refractive index for linearly polarized light with ${}^e\beta^e = \frac{1}{3} {}^e\beta_{\alpha\alpha}^e$ being the mean value of the polarizability ${}^e\beta^e(-\omega; \omega)$

$$n_T^{\text{NL}} = \frac{N}{180\varepsilon_0 n_0 k_B T} (3 {}^e\beta_{\alpha\beta}^e {}^e\beta_{\alpha\beta}^e - {}^e\beta_{\alpha\alpha}^e {}^e\beta_{\beta\beta}^e) \quad (15)$$

describes the light intensity-dependent change of the refractive index, and the other constants have the following form:

$$F_T = \frac{N}{12\varepsilon_0 n_0 k_B T} {}^e\gamma_{\alpha\beta}^e {}^e\gamma_{\alpha\beta}^e, \quad (16)$$

$$D_T = \frac{N}{30\varepsilon_0 c k_B T} ({}^e\gamma_{\alpha\beta}^m {}^e\gamma_{\alpha\beta}^m + {}^e\gamma_{\alpha\beta}^m {}^e\gamma_{\beta\alpha}^m), \quad (17)$$

$$M_T = \frac{N}{6\varepsilon_0 c k_B T} ({}^e\beta_{\alpha\beta}^m {}^e\beta_{\alpha\beta}^m - {}^e\beta_{\alpha\beta}^m {}^e\beta_{\beta\alpha}^m), \quad (18)$$

and they are related to optically induced circular and axial birefringence discussed with details in the separate paper [29]; $(\mathbf{E} \times \mathbf{E}^*)_z$ and $(\mathbf{E}^* \times \mathbf{B})_z$ in Eq. (13) denote the z -component of the vector product in the brackets. The temperature dependent parameters F_T and M_T disappear if the ground state of the molecule is non-degenerate.

On the other hand the refractive index of the linearly polarized light with the same intensity is

$$n = n_0 + n_T^{\text{NL}} |\mathbf{E}|^2 + M_T (\mathbf{E}^* \times \mathbf{B})_z. \quad (19)$$

For right (R) and left (L) c.p. light propagating in z -direction we have [29]:

$$i(\mathbf{E} \times \mathbf{E}^*)_z^{\text{L}} = -i(\mathbf{E} \times \mathbf{E}^*)_z^{\text{R}} = E^2, \quad (20)$$

$$i(\mathbf{E}^* \cdot \mathbf{B})^{\text{L}} = -i(\mathbf{E}^* \cdot \mathbf{B})^{\text{R}} = EB, \quad (21)$$

$$(\mathbf{E}^* \times \mathbf{B})_z^{\text{L}} = (\mathbf{E}^* \times \mathbf{B})_z^{\text{R}} = EB, \quad (22)$$

and, moreover, for linearly polarized light

$$(\mathbf{E}^* \times \mathbf{B})_z = EB. \quad (23)$$

The effect, which we are interested in, is described by the difference $\Delta n = n - n_{\pm}$ of the refractive indices for linearly and circularly polarized light

$$\Delta n = n - n_{\pm} = F_T E^2 + D_T EB. \quad (24)$$

In general case the nonlinear terms describing nonlinear electronic distortion should be included in Eqs. (13), (19) and (24) (see Sec. 3).

3. Discussion

For achiral molecules with non-degenerate electronic ground state the constant $F_T = 0$ and the effect depends on components of the polarizability tensor ${}^e\gamma^{\text{m}}$ containing one electric dipole and one magnetic dipole transition (the Rosenfeld polarizability) as we could expect from the torques given by Eqs. (1) and (2) (see also Eqs. (20) and (21) in Ref. [26]: the effect revealed by the FMD technique corresponds to the effect described in the present paper by the term $D_T EB$). The non-zero components of the tensor ${}^e\gamma_{\alpha\beta}^{\text{m}}$ for all point symmetries of achiral molecules are presented in Table. From Table we have

$$D_T = \frac{N}{30\varepsilon_0 ck_B T} [({}^e\gamma_{13}^{\text{m}} + {}^e\gamma_{31}^{\text{m}})^2 + ({}^e\gamma_{23}^{\text{m}} + {}^e\gamma_{32}^{\text{m}})^2] \quad (25)$$

for molecules with the point group m (C_{1h});

$$D_T = \frac{N}{30\varepsilon_0 ck_B T} ({}^e\gamma_{12}^{\text{m}} + {}^e\gamma_{21}^{\text{m}})^2 \quad (26)$$

for molecules having the symmetry $mm2$ (C_{2v});

$$D_T = \frac{2N}{15\varepsilon_0 ck_B T} ({}^e\gamma_{12}^{\text{m}})^2 \quad (27)$$

for molecules with the symmetry $\bar{4}$ (S_4). For the remaining point group symmetries of achiral molecules the constant D_T is equal to zero.

TABLE
The rank-2 axial tensor ${}^e\gamma_{\alpha\beta}^m$ for all point group symmetries of achiral molecules [27]. The point groups are given in the international notation, in brackets the Schoenflies notation.

Point group	${}^e\gamma_{\alpha\beta}^m$
$m(C_s)$	${}^e\gamma_{13}^m, {}^e\gamma_{31}^m, {}^e\gamma_{23}^m, {}^e\gamma_{32}^m$
$mm2(C_{2v})$	${}^e\gamma_{12}^m, {}^e\gamma_{21}^m$
$\bar{4}(S_4)$	${}^e\gamma_{11}^m = -{}^e\gamma_{22}^m, {}^e\gamma_{12}^m = {}^e\gamma_{21}^m$
$3m(C_{3v}), 4mm(C_{4v}), 6mm(C_{6v}), \infty m(C_{\infty v})$	${}^e\gamma_{12}^m = -{}^e\gamma_{21}^m$
$\bar{4}2m(D_{2d})$	${}^e\gamma_{11}^m = -{}^e\gamma_{22}^m$

For the remaining point groups of achiral molecules all components vanish

The above results show that the effect revealed by the FMD technique and discussed in this paper may give information on off-diagonal elements of the Rosenfeld polarizability tensor, also for non-dipolar molecules having the symmetry of the point group $\bar{4}(S_4)$, when there is no contribution of the components ${}^e\gamma_{\alpha\beta}^m$ to the linear [30] and nonlinear [31] electric Rayleigh optical activity.

As a rough estimate we take ${}^e\gamma_{12}^m \approx 10^{-34} A^2 J^{-1} m^3 s$ (in the paper [30] an experimental value for ${}^e\gamma_{12}^m$ for the molecule CH_3Cl of $-0.34 \times 10^{-34} A^2 J^{-1} m^3 s$ is given from linear electric Rayleigh optical activity measurements) and $N \approx 10^{28} m^{-3}$ which give

$$\Delta n = D_T EB \approx 10^{-26} E^2$$

with E in $V m^{-1}$. In this case the effect seems to be too small for measurement (it could be measured by focusing a giant ruby laser pulse producing a field 10^9 – 10^{10} V/m but the optical breakdown may appear). We hope that for some achiral molecules (macromolecules) with larger off-diagonal components of the Rosenfeld polarizability the effect may be observable in much lower optical field.

For achiral molecules with degenerate electronic ground state the main contribution to the difference Δn given by Eq. (24) may come from the first term $F_T E^2$. Taking ${}^e\gamma^e \approx 1.7 \times 10^{-40} C^2 m^2 J^{-1}$ [24] we have at room temperature

$$\Delta n \approx 1.5 \times 10^{-21} E^2,$$

where E is in SI units. The effect might be detectable even for the field $E \approx 10^7$ V/m which corresponds to the light intensity of 10^{11} W/m².

We would like to notice that, in general, when the nonlinear electronic distortion is taken into consideration, the expressions for the indices n_{\pm} , n and Δn have the form of Eqs. (13), (19) and (24) with the constants $n^{NL} = n_0^{NL} + n_T^{NL}$, $F = F_0 + F_T$, $D = D_0 + D_T$ and $M = M_0 + M_T$ instead of n_T^{NL} , F_T , D_T and M_T , and the new constants contain, besides the temperature-dependent terms, also the temperature-independent terms (denoted by the subscripts "0") related to nonlinear interaction of molecules with the radiation [29]. For anisotropic molecules the temperature-dependent terms (if they are not equal to zero because of molecular

symmetry) are usually much larger than the respective terms describing the non-linear electronic distortion [24, 29] and in such case the temperature-independent terms may be neglected. Since, moreover, $F_0 E^2 \gg D_0 EB$ [29] we have for molecules with non-degenerate electronic ground state

$$\Delta n = n - n_{\pm} = F_0 E^2 + D_T EB, \quad (28)$$

with

$$F_0 = \frac{N}{16\epsilon_0 n_0} [{}^e\beta_{\alpha\beta\beta\alpha}^{eee}(-\omega; \omega, -\omega, \omega) - {}^e\beta_{\alpha\beta\alpha\beta}^{eee}(-\omega; \omega, -\omega, \omega)], \quad (29)$$

which is non-zero for all atoms and molecules. The quantum mechanical form of the hyperpolarizability ${}^e\beta_{\alpha\beta\gamma\delta}^{eee}(-\omega; \omega, -\omega, \omega)$ is given in Ref. [29].

As a rough estimate of the constant F_0 we take ${}^e\beta^{eee} \approx 10^{-60} C^4 m^4 J^{-3}$ which is typical for such molecules as C_2H_6 , C_6H_6 , CS_2 [5] and which leads to $F_0 \approx 10^{-22} m^2 V^{-2}$. The above estimation means that the contribution of the term $F_0 E^2$ to the effect discussed in this paper may be observable for c.p. light with the amplitude of the electric field $E \approx 10^8$ V/m.

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